Colloids and Surfaces A: Physicochem. Eng. Aspects 422 (2013) 10–18

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Studying of 1-D assemblies in anionic azo dyes and cationic surfactants mixed systems

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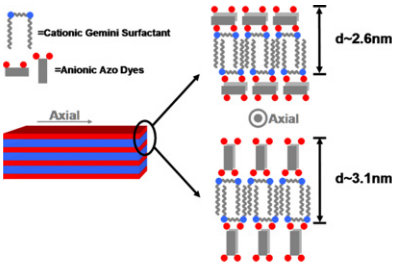
HIGHLIGHTS

- 1-D structures were found in azo dyes and cationic surfactants mixed systems.
- Helixes were found in one of the mixed systems.
- The regulation of the formation of these 1-D structures has been investigated.

GRAPHICAL ABSTRACT

Combination of steric effect, π–π stacking, electrostatic and hydrophobic interaction, the packing model of dye and surfactant molecules in the 1-D nano-structures has been suggested.



ARTICLE INFO

Article history:
Received 12 November 2012
Received in revised form
17 December 2012
Accepted 20 December 2012
Available online 11 January 2013

Keywords:
One-dimensional
Self-assembly
Gemini surfactants
Azo dyes

ABSTRACT

The construction and regulation of one-dimensional (1-D) structure have been fully investigated in anionic azo dyes and cationic surfactants mixed systems. Anionic azo dyes with different charge numbers and different size of conjugated groups were selected. Analogously, cationic alkyl quaternary ammoniums surfactants with different chain length, charges on the head, and types of the surfactants were tested. By studying the relationship between molecular structure and intermolecular interactions in a controlled way, it was found that 1-D self-assembly is a process that affected by multiple interactions, including electrostatic attractions, hydrophobic interactions, and potential π–π staking. Besides, the symmetry of the molecules also affects the morphology of the assemblies.

1. Introduction

Recently, one-dimensional (1-D) nano-structures have received an intensive attention owing to their superior electronic [1–6], optical [7–9], sensing [10–12], and energetic [13] properties resulted from the quantum-confinement effects and high surface area to volume ratio, and are expected to be applied in biological sensing [14] and disease diagnoses [15–18]. So far, many attempts have been made to achieve 1-D nano-structures such as vapor deposition [19], solution–liquid–solid method [20], template-directed methods [21–24], and molecular self-assembly [25–30]. Among these, self-assembly in aqueous solution is a simple and mild way to construct 1-D nano-structures since it allows rational control of the shape and size of 1-D nano-structures. Combining the non-directional interactions such as electrostatics, solvophobicity, directional forces such as coordination binding, hydrogen bonding, and π–π stacking, via molecular design, one may obtain, well-defined 1-D structures with different properties [31]. Typical examples are 1-D nano-structures assembled from conjugated

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0927-7757/$ – see front matter
http://dx.doi.org/10.1016/j.colsurfa.2012.12.062

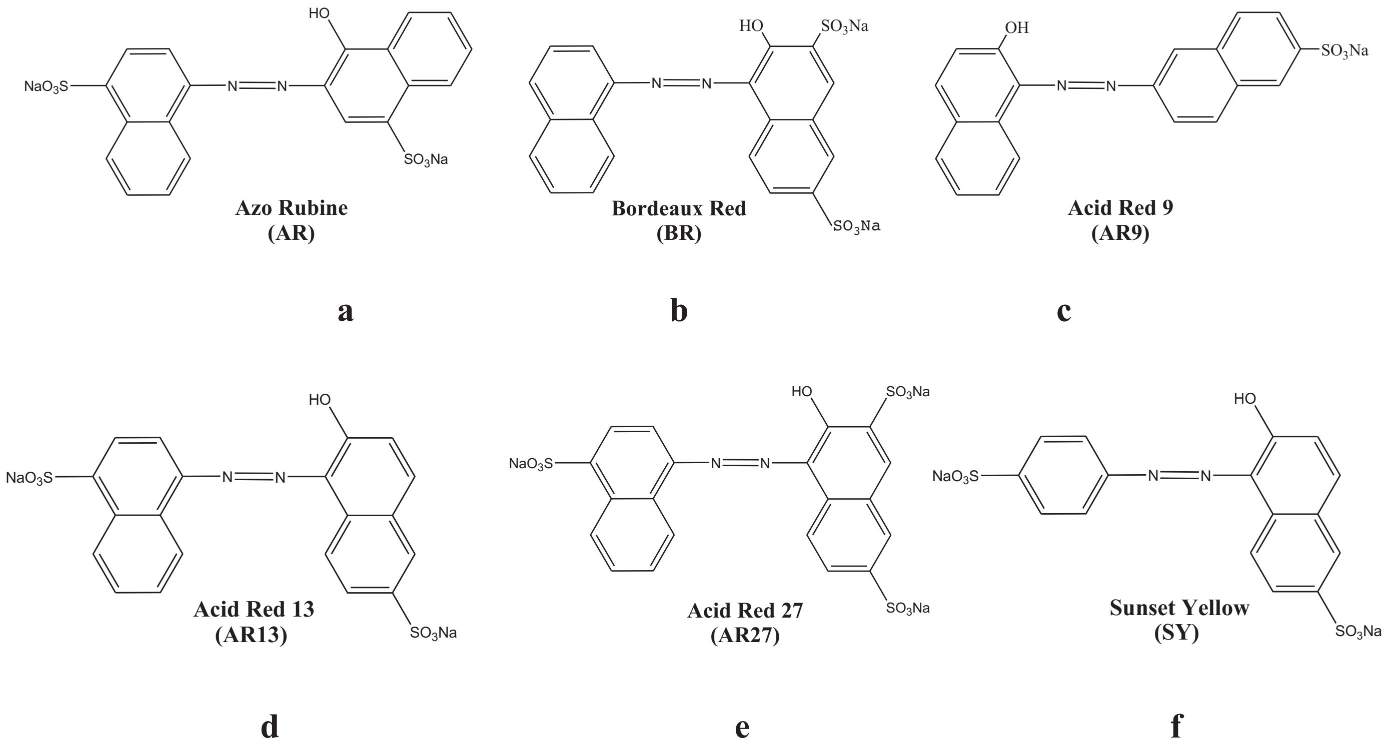

Fig. 1. Schemes of chemical ctructure of azo-dyes.

disk-like molecules or dyes, where the symmetry and π–π interactions among the conjugated groups define the orientation of 1-D self-assembly. For example, Shelnutt reported the formation of nano-fibers by two oppositely charged porphyrins in aqueous solution [32]. Faul studied the formation of nanotubes by two oppositely charged dyes with different frame structure (porphyrins and perylenes) [33]. Besides, dyes (often carrying negative charges) were also co-assembled with surfactants or other molecules via electrostatic interaction, hydrogen bonding and coordination interaction to construct 1-D nano-structures. For instance, Burger achieved ribbon-like aggregates by perylenetetracarboxylic dianhydride, which has a negative charged perylene frame structure and optical ionic of quaternary ammonium with two hydrophobic chains [34]. Similarly, Hoffmann reported the formation of nano-fibers in the mixed systems of dyes and surfactants, where the morphology of the fibers was controlled by the mixed ratio [35]. Fine-tune of the 1-D self-assembled structures were achieved by Faul and co-workers, through introduction of the hydrogen bonding [36], coordinating [37], and chiral centers into the surfactants [38]. In our recent studies, nano-fibers were constructed in different systems, including the mixed system of an aromatic anionic surfactant and oppositely charged aromatic hydrotropic salt [26], the mixed system of negative charged bile salts and various metal ions [30], and azo-modified surfactants with head groups of dipeptide [27] and glycosylamine [28]. The driving forces in these systems are including electrostatic attraction, hydrophobic interactions, π–π interactions, coordination interactions and hydrogen bonds.

In spite of the elegant studies on the aforementioned 1-D nanostructures based on dyes, the role of non-covalent interactions that participate in the assembling process is still lack of systematic study. This work aims to establish the relation between the molecule structure and the morphology of the self-assemblies, and to understand the role of non-covalent interactions on the formation of 1-D self-assembly. To this end, 1-D assemblies formed in a series of mixed systems of azo dyes and surfactants were studied. The dyes have similar structures (Fig. 1) which differ either in charge numbers, or in the size of aromatic rings. Analogously, the structure of the cationic surfactant was also varied in a rationally controlled way, including changing the chain length, the charges on the head, as well as varying the type of the surfactants, namely from classical to Gemini with spacers of various length. Upon considering these structural factors one by one, we are able to obtain a systematic knowledge about the role of head group sizes, charge density matching, π–π interactions, and hydrophobic interactions on the 1-D structure formation.

2. Materials and methods

2.1. Materials

Acid Red 13 (AR13), Acid Red 27 (AR27), Azo Rubine (AR), Sunset Yellow (SY), Acid Red 9 (AR9) and methyl orange (MO) were purchased from TCI. Bordeaux Red (BR) was from Acros Organics Co. Dodecyltrimethylammonium bromide (DTAB), sodium dodecylsulfate (SDS) and *p*-octyl polyethylene glycol phenyl ether (Triton X-100) were from Alfa Aesar. All these chemicals were used as received. Quaternary ammonium bromides were prepared by reaction of 1-bromododecane and the corresponding trialkylamine as described in our previous paper. The abbreviations of the quaternary ammonium bromides are listed as follows: dodecyltriethylammonium bromide (DEAB); dodecyltripropylammonium bromide (DPAB); octyltributylammonium bromide (OTAB); decyltributylammonium bromide (DeTAB); dodecylpyridinium bromide (DPyB) and dodecylmethylimidazolium bromide (DMImB). The Gemini surfactants alkylene-a,s-bis(dodecyldimethylammonium bromide) (12-s-12(Me)) (s = 4\6\10) were synthesized in this lab according to the procedure reported elsewhere [39]. Milli Q water was used throughout this work. All other reagents were products of A.R. grade.